

RCE Response  
U.S.S.N. 09/890,290  
Page No. 12

### REMARKS

In view of the Examiner's comments regarding the Applicants' attempt to incorporate subject matter into this application by reference to U.S.S.N. 60/117,852 in page 13 of the specification, the present amendment has copied the essential information from the provisional application for insertion into the present application.

The Examiner should note that a related application – U.S.S.N. 10/436,944, which claims priority to the '852 provisional application, has been published as U.S. Pat. Pub. No. 2003-0201223 A1. A search of the PTO "PAIR" database for U.S.S.N. 60/117,852 leads one to this published application.

Applicants understand that the claimed invention remains rejected under Section 102(b) or 103(a) as being unpatentable over the teachings of Kawai et al. (U.S. Patent No. 5,158,680). This rejection is respectfully traversed. The basis for this rejection is the following statement, from the Advisor Action:

Since the applicant's process and Kawai process are similar (phase inversion), and both use similar materials, Kawai also is inherently expected to have structure similar to what is depicted in the Fig 7 (or for that matter, 5, 6, 8, etc.) of WO 00/44484.

The premise of this rejection is simply incorrect. As taught and claimed herein, the invention includes perfluorinated thermoplastic hollow fiber membranes formed by thermally induced phase separation and liquid-liquid phase separation. See the following language from U.S.S.N. 60/117,852 (now as published in Pub. No. 2003-0201223):

RCE Response  
U.S.S.N. 09/890,290  
Page No. 13

A person of ordinary skill in the art of making porous membranes will find it possible to use the teachings of the present invention to produce essentially skin-free hollow fiber porous membranes from perfluorinated thermoplastic polymers **which can be dissolved in a solvent** to give a solution having an upper critical solution temperature, and which when the solution is cooled, separates into two phases by liquid-liquid phase separation.

In contrast thereto, the Kawai invention does not utilize a solution process. It uses a dispersion of particles of PTFE resin material (either aqueous or organic) in which the particles have a size not greater than 1 micron, preferably not greater than 0.8 micron. See Col. 3, lines 53-62 of the '680 patent. This is consistent with the language of claim 1 of the patent, which recites "A porous film membrane consisting essentially of a layer of a porous polytetrafluoroethylene resin **particle bond structure** substantially devoid of a fibrillated portion". (emphasis added)

The processes are different. There is no teaching or suggestion in Kawai to switch from the dispersion process to the presently claimed solution process. Accordingly, Kawai neither teaches nor suggests the invention of the present claims, and the rejection citing this reference should be reconsidered and withdrawn. Such action is respectfully requested.

The proposed combination of Kawai and EP '432 does not overcome the deficiency of the primary reference. Kawai remains a dispersion process, which produces a product having "a particle bond structure" which neither teaches nor suggests the structures formed by the thermally induced phase separation and liquid-liquid phase separation process claimed herein.

RCE Response  
U.S.S.N. 09/890,290  
Page No. 14

Reconsideration and withdrawal of the Section 103(a) rejection citing Kawai and EP '432 is respectfully requested.

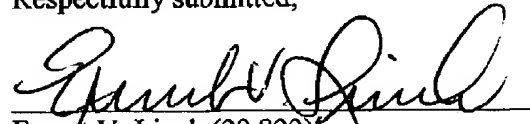
**FEE AUTHORIZATION**

Please charge all fees (excess claim fees, time extension fees) associated with this filing to our Deposit Account – No. 19-0733.

**CERTIFICATE OF FACSIMILE TRANSMISSION**

The undersigned hereby certifies that this correspondence was submitted by facsimile in the USPTO on the date shown on Page 1.

Respectfully submitted,

A handwritten signature in cursive script, appearing to read "Ernest V. Linek", written over a horizontal line.

Ernest V. Linek (29,822)  
Attorney for Applicant

Document No. 100936

quenching of the surfaces. Third, the hot oil tends to soften the extruded melt and the extruded fiber tends to break apart during processing.

Post-stretching was disclosed as another technique to enhance permeability of a skinned PFA membrane in US Patents 4,990,294, and 5,032,274. While stretching does increase permeability substantially, it produces its own set of undesirable side-effects. First, for stretching to be effective, the base skinned membrane must be very uniform in thickness and in mechanical strength. Any non-uniformity in the base membrane will be amplified as soon as the membrane is subjected to stretching, because weak areas stretch more than strong areas under the same stretching force. As mentioned above, it is very difficult to produce base membranes with the solvent coating technique. If solvent coating is not used, the heavy evaporation of porogen usually produces dried polymer on the die lips. This accumulated dried polymers then scratch the melt surfaces, producing lines of hidden weaknesses in the base membrane. Upon stretching, the weakened membranes would break apart along the "scratch" lines.

It would therefore be desirable to have a process that would eliminate the rapid evaporation of solvent from the fiber surface, but not require a difficult coating or stretching step. It would also be beneficial to produce a skinless membrane having high surface porosity in order to utilize a large proportion of the membrane surface for permeation and retention.

#### Summary of the Invention

This invention provides for high flux, skin-free hollow fiber porous membranes, more specifically, microporous membranes, from perfluorinated thermoplastic polymers, more specifically poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) (POLY(PTFE-CO-PFVAE)) or poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP). These membranes are capable of operating in severe chemical environments with no apparent extractable matter being released. Compared to prior art membranes, the membranes of the invention have a higher surface porosity, which translates into high permeability or flux.

A process to produce these membranes is provided. The process is based on the Thermally Induced Phase Separation (TIPS) method of making porous

\*  
60117857.012999

structures and membranes. A mixture of polymer pellets, usually ground to a size smaller than supplied by the manufacturer, and an solvent, such as chlorotrifluoroethylene oligimer, is first mixed to a paste or paste-like consistency. The polymer comprises between approximately 12% to 35% by weight of the mixture. The solvent is chosen so the membrane formation occurs by liquid-liquid, rather than solid-liquid phase separation when the solution is extruded and cooled. Preferred solvents are saturated low molecular weight polymers of chlorotrifluoroethylene. A preferred solvent is HaloVac® 60 from Halocarbon Products Corporation, River edge, NJ. Choice of the solvent is dictated by the ability of the solvent to dissolve the polymer when heated to form an upper critical solution temperature solution, but not to excessively boil at that temperature. Fiber extrusion is referred to as spinning and the extruded fiber length from the die exit to the take-up station is referred to as the spin line. The paste is metered into a heated extruder barrel where the temperature raised to above the upper critical solution temperature so that dissolution occurs. The homogeneous solution is then extruded through an annular die directly into a liquid cooling bath with no air gap. The liquid cooling bath is maintained at a temperature below the upper critical solution temperature of the polymer solution. The preferred bath liquid is not a solvent for the thermoplastic polymer, even at the extrusion temperature. Upon cooling, the heated and shaped solution undergoes phase separation and a gel fiber results. The die tip is slightly submerged for vertical spinning, i.e., the spin line falls downward, in the direction of a freely falling body. For horizontal spinning, where the spin line exits directly in the horizontal attitude, and is maintained more or less in that plane until at least the first guide roll, a specially design die is used. The die is firmly positioned against an insulated wall with the die tip penetrating through a opening having a liquid-tight seal in the insulator wall. A trough for cooling liquid flow is placed in a recess in the opposite side of the insulating wall, in a manner that will maintain the die nose outlet in a submerged condition. Cooling liquid flows in the trough and overflows in a region of the trough of lesser depth, keeping the die nose outlet submerged with a flow of cooling liquid. In both the vertical and horizontal methods, a booster heater and temperature control means is used to briefly raise the solution temperature at the die tip to prevent premature cooling. In a subsequent step, the dissolution

solvent is removed by extraction and the resultant hollow fiber membrane is dried under restraint to prevent membrane shrinkage and collapse. Optionally the dried fiber may be heat set at 200°C to 300°C.

#### Brief Description of the Drawings

Figure 1 is a flow diagram of the process of this invention with vertical extrusion.

Figure 2 is a flow diagram of the process of this invention with horizontal extrusion.

Figure 3 is a drawing of the die used in vertical fiber spinning.

Figure 4 is a drawing of the die used in horizontal fiber spinning.

Figure 5 is a photomicrograph at 3191X of the inner surface of a hollow fiber microporous membrane made from poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) made in accordance with Example 1, Sample #3.

Figure 6 is a photomicrograph at 3191X of the outer surface of a hollow fiber microporous membrane made from poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) made in accordance with Example 1, Sample #3.

Figure 7 is a photomicrograph at 3395X of the inner surface of a hollow fiber microporous membrane made from poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) made in accordance with Example 1, Sample #8.

Figure 8 is a photomicrograph at 3372X of the outer surface of a hollow fiber microporous membrane made from poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) made in accordance with Example 1, Sample #8.

Figure 9 is a photomicrograph at 984X of the inner surface of a hollow fiber microporous membrane made from poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP), made in accordance with Example 5.

Figure 10 is a photomicrograph at 1611X of the outer surface of a hollow fiber microporous membrane made from poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP), made in accordance with Example 5.